

NITROGEN COMPOUND TYPES IN GREEN RIVER OIL SHALE AND ITS KEROGEN DEGRADATION PRODUCTS

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INTRODUCTION

Information about the nitrogen compounds in oil shale and oil-shale degradation products is needed in order to provide more efficient processes for converting oil shale to useful energy with minimum environmental contamination. At present very little is known about the types of nitrogen compounds present in the soluble extracts that can be obtained from oil shale or the types of nitrogen compounds that are formed when previously extracted oil-shale samples are heated for prolonged periods at temperatures below those usually employed in retorting.

Some research has been done on the nitrogen compounds in shale oil and oil shale. Smith and coworkers¹ separated a shale-oil distillate boiling above 400° F on Florisil into hydrocarbon and nonhydrocarbon nitrogen-containing fractions. Haines and coworkers² published techniques for separating and identifying nitrogen compounds in petroleum and shale oil. Decora and Dinneen⁴ developed a gas-liquid chromatography method, based on using detergent as the solid phase, for separating basic nitrogen compounds in shale oil. Dinneen⁵ identified pyridines, indoles, quinolines, and tetrahydroquinolines in shale oil. Moore and Dunning⁶ isolated the porphyrins from oil-shale extracts and determined that they were complexed with iron and nickel. Anders and Robinson¹ studied the polar constituents isolated from Green River oil shale and found that alkoxy-pyrrolines, alkylmaleimides, tetrahydroquinolines, and quinolines were present in the polar material. Morandi and Jensen⁹ compared the porphyrins from a shale-oil fraction, oil-shale extract, and a petroleum fraction. They found that the porphyrins in oil shale are a complex mixture of etio-type porphyrins in the 366 to 522 molecular-weight range. Simoniet and coworkers¹³ studied nitrogenous compounds of the Green River Formation and found quinoline, indole or pyridine, and tetrahydroquinoline present in their oil-shale extracts.

The object of this research was to increase our knowledge about the effect of depth of burial on the nitrogen compounds present in Green River oil shale and to determine what types of nitrogen compounds are formed when oil shale is heated at temperatures in the range of 150° to 350° C for periods from 0.5 to 360 days. The present paper describes the results obtained for nitrogen compound-type analysis of fractions of the complex high-molecular-weight oil-shale products. In the study of extracts from the oil-shale core samples, an attempt was made to relate the analytical data to depth of burial and to determine if depth of burial affects the type of nitrogen compounds present in the extracts. In addition, the effect on oil-shale nitrogen structures due to long-time heating at low temperatures similar to that experienced peripherally to in situ retorting operations was determined.

EXPERIMENTAL PROCEDURES

The samples used in this study were obtained from two previous oil-shale studies. The extracts (soluble bitumen) obtained from a core of the Green River Formation are the same as described in a report by Robinson and Cook¹² on the 2,300-foot Colorado No. 1 core. The low-temperature thermal products (pyrolytic bitumen) are the same as those described by Cummins and Robinson³ where previously extracted 66-gpt oil shale from the Bureau of Mines' demonstration

mine at Rifle, Colorado was heated at temperatures ranging from 150° to 350° C for periods ranging from 0.5 to 360 days. The samples were fractionated into acid, bases, neutral-nitrogen, aromatic, and saturate compounds by a fractionation scheme. Each of the various fractions were analyzed for strong bases, weak bases, very weak bases, and nontitratable nitrogen by potentiometric titration. No attempt was made to distinguish between titratable nitrogen compounds and titratable nonnitrogen compounds; however, the latter type has been found by Poulson¹¹ to be insignificant in shale-oil products.

Product Fractionation

The samples used in this study are high-molecular-weight complex materials; however, they are amenable to a fractionation and separation scheme devised by Jewell, et al.⁷ Figure 1 shows the fractionation scheme used and the fractions that resulted.

The acid and base fractions are removed with Amberlyst A-29 anion- and Amberlyst 15 cation-exchange resins, while the neutral nitrogen fraction is removed by coordination-complex formation with ferric chloride supported on Attapulugus clay. Most of the nitrogen compounds are removed as acid, base, and neutral nitrogen fractions. The remaining hydrocarbon material was separated into aromatic and saturate fractions by adsorption chromatography on a column of Davison grade 12 silica gel.

Analyses of Fractions

The concentration of nitrogen present in the original samples and in the acid, base, neutral nitrogen, aromatic, and saturate fractions of these samples was determined using a system consisting of a reductive-nickel pyrolysis tube which directed the pyrolyzed product to an ammonia micro-coulometer. Samples were introduced through a boat inlet into the pyrolysis tube. Types of nitrogen compounds present in the fractions were determined using published methods by Streuli¹⁵ and Nicksic.¹⁰ No attempt was made to identify individual nitrogen compounds in this research. Nitrogen compounds referred to in this report are based on Buell's² published classification results.

RESULTS AND DISCUSSION

The nitrogen content was determined for samples obtained either by extracting portions of Colorado No. 1 core or by thermally degrading oil-shale kerogen. The nitrogen content of the oil-shale core extracts range from 0.11 to 0.82 percent, and the thermal degradation products ranged from 1.36 to 2.22 percent. On an average basis, the thermal product contains 2.7 times more nitrogen than the core extracts.

The distribution of the fractions obtained from Colorado No. 1 core extracts is shown in table 1. All the fractions contain more hydrocarbon (aromatic plus saturated) material than polar (acid, base, and neutral nitrogen) material except sample No. 7. The base-to-acid ratio remains at about one except for samples Nos. 24, 58, and 59. The base-to-neutral nitrogen ratio remains at about one except for samples Nos. 7, 24, and 58. The highest ratio of base-to-acid or base-to-neutral occurs in sample No. 58. The most hydrocarbons appear in the two samples at the bottom of the core. This generalization agrees with the results published by Robinson and Cook.¹² The average percents show that the polar materials are equally divided between the acid, base, and neutral nitrogen fractions. The various amounts of loss are probably complex high-molecular-weight materials generally insoluble in the solvents used in the fractionation scheme.

The distribution of fractions of kerogen thermal degradation products appears in table 2. The amount of aromatic and saturate fractions range from 37.7 to 60.0 percent of the total thermal

TABLE 1. - Distribution of the fractions obtained from Colorado No. 1 core extracts

Sample No.	Depth of burial, ft	Fraction, weight percent of total product					
		Acid	Base	Neutral-N	Aromatic	Saturate	Loss
5	943.7- 947.4	12.0	12.0	13.2	22.0	33.2	7.6
6	989.5- 990.5	11.7	10.5	9.3	22.1	30.7	15.7
7	995.4- 998.1	21.1	16.9	10.3	19.4	23.6	8.7
9	1,076.3-1,079.9	13.2	12.6	10.2	24.4	30.3	9.3
17	1,399.8-1,401.3	11.3	11.1	10.4	29.3	27.7	10.2
20	1,539.5-1,541.0	14.9	11.6	11.1	26.2	36.1	.1
24	1,696.1-1,697.1	6.0	10.8	23.1	29.3	23.2	7.6
58	3,039.0-3,040.3	4.2	12.8	7.0	20.2	40.6	15.2
59	3,065.1-3,071.2	2.3	4.8	5.8	17.9	66.8	2.4
Average		10.7	11.5	11.2	23.4	34.7	8.5

TABLE 2. - Distribution of fractions of kerogen thermal degradation products

Heating time, days	Temperature °C	Fraction, weight percent of total product					
		Acid	Base	Neutral-N	Aromatic	Saturate	Loss
360	150	12.4	15.4	17.0	21.2	16.5	17.5
90	200	7.9	11.3	10.6	25.5	27.9	16.8
12	250	17.2	21.2	7.1	24.3	19.6	10.6
4	300	8.3	23.2	6.3	34.0	26.0	2.2
0.5	350	9.1	25.3	15.7	34.4	7.5	8.0
Average		11.0	19.3	11.3	27.9	19.5	11.0

product. Three fractions contain less than 50 percent hydrocarbon material (aromatic and saturate). All the thermal products contain higher proportions of base than acid material. On an average basis, about the same amounts of acid and neutral material are present. The amount of aromatic material generally increases with temperature from 150° to 350° C and on an average is about 1.4 times the amount of either the saturate or base material. The percent loss tends to decrease with increased temperature as the complex materials are thermally degraded to lower-molecular-weight and more soluble materials.

The nitrogen content of fractions of the core extracts appears in table 3. As expected, most of the nitrogen is concentrated in the polar fractions, and the largest amount of nitrogen always appears in the base fraction. Samples Nos. 58 and 59 have base-to-acid nitrogen ratios ranging from 7 to 9.5 compared to an average of about 1.9 for samples 5 through 24. Also, samples Nos. 58 and 59 have base-to-neutral nitrogen ratios of 7 to 15 compared to an average of about 3 for samples Nos. 5 through 24. These results suggest some form of diagenetic process at the bottom of the core similar to that expected by thermal alteration.

Nitrogen content of fractions of the kerogen thermal degradation products appears in table 4. Most of the nitrogen appears in the base fractions as it did in the oil-shale core extracts. On an average basis, aromatic fractions contain about 2.5 times more nitrogen than the comparable core fraction while the saturate fractions are approximately equal. The ratios of nitrogen in the base fractions relative to the acid and neutral nitrogen for thermal products prepared at 200° C and above are high. They range from about 5 to 10 in regard to base-to-acid nitrogen ratio and

TABLE 3. - Nitrogen content of fractions of the core extracts

Sample No.	Nitrogen content, weight percent of total nitrogen					
	Acid	Base	Neutral-N	Aromatic	Saturate	Loss
5	25.8	42.8	15.0	4.5	3.4	8.5
6	23.2	39.7	13.9	2.9	3.2	17.1
7	19.8	40.6	10.9	1.9	1.2	25.6
9	24.7	55.8	11.1	3.4	3.1	1.9
17	22.1	42.8	20.0	5.0	3.5	6.6
20	24.8	29.7	19.2	6.6	4.6	15.1
24	12.4	38.7	8.5	5.6	5.6	29.2
58	5.1	48.7	3.3	9.6	13.9	19.4
59	9.0	63.6	9.0	9.0	9.0	.4
Average	18.5	44.7	12.3	5.4	5.3	13.8

TABLE 4. - Nitrogen content of fractions of the kerogen thermal degradation products

Heating time, days	Temperature °C	Nitrogen content, weight percent of total nitrogen					
		Acid	Base	Neutral-N	Aromatic	Saturate	Loss
360	150	14.9	26.7	6.2	4.3	2.5	45.4
90	200	7.0	33.6	9.9	9.6	5.5	34.4
12	250	15.4	46.0	7.1	10.2	5.4	15.9
4	300	2.7	26.7	4.1	12.2	7.2	47.1
0.5	350	5.6	38.0	9.8	25.4	3.6	17.6
Average		9.1	34.2	7.4	12.3	4.8	32.2

from about 3 to more than 6 for the base-to-neutral nitrogen ratio. These results are roughly similar to the results obtained on samples Nos. 58 and 59 of the core fractions (table 3) showing the change expected by thermal alteration.

The distribution of nitrogen-compound types present in fractions of the core extracts appears in table 5. Four different nitrogen-compound types were determined and are as follows: Strong bases, weak bases, very weak bases, and nontitratable nitrogen compounds. Contrary to what one would expect, strong base compounds appeared in the neutral nitrogen fractions. The separation method used should have retained any strong bases on the cation resins. One possible reason for the presence of strong bases in this fraction may be steric hindrance and molecular shape. Nitrogen compounds such as highly alkylated substituted pyridines could pass through the cation resin. No strong bases appear in any of the other fractions. All of the acid and base fractions contain both weak and very weak base type nitrogen compounds. Quinolines, hindered pyridines, and phenanthridines may be present in the weak-base type of nitrogen compounds. Weak bases are present in both the neutral nitrogen samples Nos. 6 and 17 and in saturate sample No. 9. All of the fractions except aromatic fraction No. 17 and saturate fractions Nos. 7 and 9 contain very weak base type nitrogen compounds. Very weak base type compounds could be anilines and certain acridines which acetylate and titrate as amides in acetic anhydride. All of the acid and aromatic fractions, three of the base fractions, one of the neutral nitrogen fractions, and two of the saturate fractions contain nontitratable nitrogen compounds. Nontitratable nitrogen-type compounds could be certain multiring pyrrolic nitrogen compounds, amides, or diamides that are partially or completely insoluble in acetic anhydride. Also, other high-molecular-weight insoluble materials in these fractions of the extracts could account for some of the titratable nitrogen type.

TABLE 5. - Distribution of nitrogen-compound types present in fractions of the core extracts

Sample No.	Nitrogen content, relative weight percent of total nitrogen			
	Strong base	Weak base	Very weak base	Nontitratable nitrogen
<u>Acid fraction</u>				
5	<1	4	6	90
6	<1	4	5	91
7	<1	4	5	91
9	<1	29	57	14
17	<1	46	46	8
<u>Base fraction</u>				
5	<1	6	6	88
6	<1	6	5	89
7	<1	5	4	91
9	<1	39	61	<1
17	<1	56	44	<1
<u>Neutral nitrogen fraction</u>				
5	33	<1	67	<1
6	<1	26	74	<1
7	14	<1	86	<1
9	32	<1	68	<1
17	<1	10	23	67
<u>Aromatic fraction</u>				
5	<1	<1	9	91
6	<1	<1	21	79
7	<1	<1	11	89
9	<1	<1	9	91
17	<1	<1	<1	100
<u>Saturate fraction</u>				
5	<1	<1	100	<1
6	<1	<1	100	<1
7	<1	<1	<1	100
9	<1	100	<1	<1
17	<1	<1	26	74

In general, the results show that most of the nitrogen compounds in the various fractions of the extracts from Colorado No. 1 core consisted of very weak bases or nontitratable nitrogen compounds. Some fractions contained weak bases and there was some evidence of strong bases in the neutral nitrogen fraction but generally the nitrogen components were of the less basic forms.

The distribution of nitrogen-compound types present in the kerogen thermal degradation products shown in table 6 are similar to that obtained for the core extracts in that most of the nitrogen-type compounds in the acid and base fractions appear in the weak base and very weak base class. Only the 360-day, 150° C saturate fraction contained strong base nitrogen compounds. This material must consist of high-molecular-weight hindered nitrogen compounds that did not react with the resins or with the silica-gel during the separation. Most of the nitrogen-type compounds in the neutral nitrogen fractions appear as nontitratable nitrogen; however, about half of the nitrogen in the 90-day, 200° C sample is very weak base type nitrogen as would be expected

TABLE 6. - Distribution of nitrogen-compound types present in fractions of the kerogen thermal degradation products

Heating time, days	Temperature, °C	Nitrogen content, relative weight percent of total nitrogen			
		Strong base	Weak base	Very weak base	Nontitratable nitrogen
<u>Acid fraction</u>					
360	150	< 1	35	65	< 1
90	200	< 1	51	29	20
<u>Base fraction</u>					
360	150	< 1	44	56	< 1
90	200	< 1	71	29	< 1
<u>Neutral nitrogen fraction</u>					
360	150	< 1	16	< 1	84
90	200	< 1	< 1	46	54
<u>Aromatic fraction</u>					
360	150	< 1	< 1	5	95
90	200	< 1	< 1	80	20
<u>Saturate fraction</u>					
360	150	62	< 1	< 1	38
90	200	< 1	< 1	9	91

by our separation scheme. One aromatic fraction contained 80 percent very weak base nitrogen compounds and two aromatic fractions contained more than 90 percent nontitratable nitrogen-type compounds.

In general, the results for the kerogen thermal degradation product were about the same as those obtained for the extracts from the oil-shale core samples. Most of the nitrogen compounds consisted of very weak bases or nontitratable nitrogen compounds; however, weak bases predominate in two of the fractions. One saturate fraction contained predominantly strong base; but, in general, most nitrogen compounds were of the less basic forms.

SUMMARY

Most of the nitrogen compounds in the extracts from oil-shale core samples and in the kerogen thermal degradation products consisted of very weak bases or nontitratable nitrogen. There was some evidence of strong bases and weak bases in some of the fractions, but generally the nitrogen-compound types consisted of the less basic forms. Basic nitrogen components were the most extensive at the greatest depth of burial for the core extracts, suggesting alteration to more basic forms of nitrogen compounds similar to those found in shale-oil products. The results of nitrogen-compound type analysis for the kerogen thermal degradation products prepared at 150° and 200° C were about the same as those obtained from extracts from the oil-shale core samples. Additional analyses will have to be made in order to determine the effect of increased temperature upon the nitrogen compound-type distribution.

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Reference to specific trade names does not imply endorsement by the Bureau of Mines.

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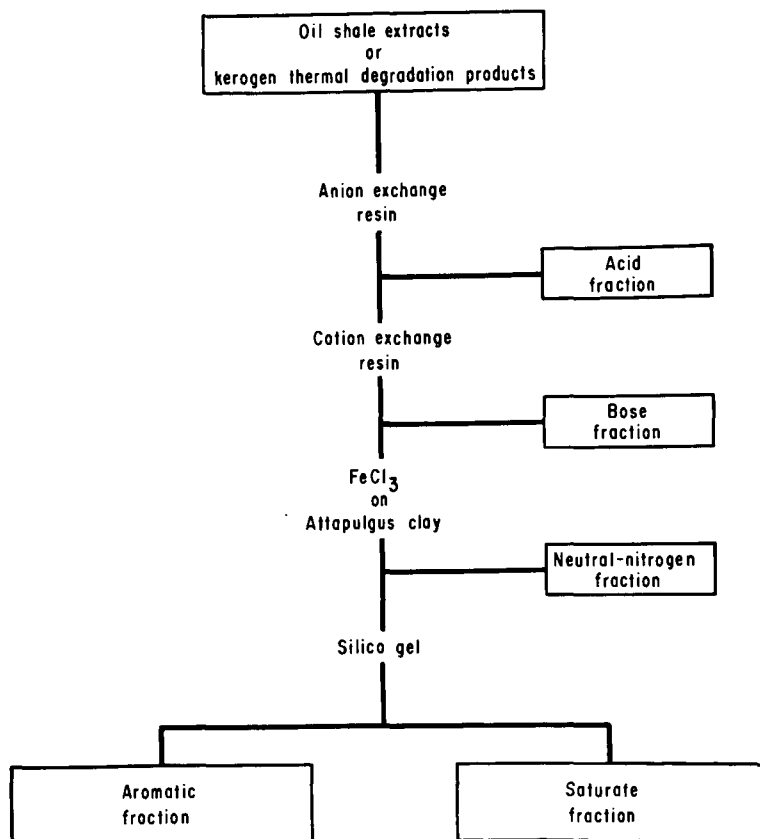


FIGURE I.-Fractionation scheme.